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Influence of Nano Al_2O_3 Particles on the Adhesion, Hardness and Wear Resistance of Electroless NiP Coatings

S. Karthikeyan and L.Vijayaraghavan

***Abstract*—In this present study electroless NiP coatings and NiP-Al_2O_3 coatings had been deposited on a mild steel substrate. The surface morphology of both the coatings had studied using scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction technique. Adhesion, hardness and wear behavior were investigated and compared for NiP and NiP-Al_2O_3 coatings. Optical micrograph images were used for the evaluation of adhesion of coatings which found sufficient and acceptable according to VDI 3198 standard. Hardness of the coating had been evaluated based on depth sensing techniques and substrate effect had avoided by maintaining depth to coating thickness ratio less than 0.1. Due to co-deposition of Al_2O_3 particles the hardness of NiP coatings increased by 20.5% (7.8 GPa to 9.4 GPa). Dry sliding wear tests were conducted on PLINT TE66 micro scale tester against steel ball of hardness 800 HV. Wear resistance of NiP coatings increased with increase in sliding distance. The co-deposition of Al_2O_3 particles in NiP matrix arrest the deformation during sliding of steel ball and thus wear resistance of NiP-Al_2O_3 coatings is superior to NiP coatings. Wear crater morphology were studied using SEM and EDS. Adhesive wear mechanics was observed in NiP coatings and combination of adhesive and abrasive wear mechanism were found in NiP-Al_2O_3 coatings.**

***Index Terms*—Adhesion, electroless coatings, hardness, wear resistance.**

I. INTRODUCTION

Coatings are used in improving the surface properties without altering the bulk property of engineering components. Chrome plating is one of the coating process which has extensive wear resistance [1] and corrosion resistance with few micrometer thickness [2]. But the usage of hexavalent chromium has been forbidden in the metal finishing industries due to environmental protection and pollution prevention [3]. To overcome these pollution problems various metals like nickel, tin, zinc, copper and brass has been used in engineering industries. Among these elements nickel based coatings play a major role in our everyday lives for decorative and industrial applications. Low temperature heat treatment of nickel coatings resulted higher wear resistance which equal or exceeds that of hard chromium coatings [4]. Properties such as corrosion resistance, better strength at high and low temperature, high hardness [5] and high wear resistance make nickel a suitable candidate for mechanical parts subject to abrasion and erosion. Apart from mechanical application nickel coatings are used in the computer industry for storage and retrieval of information on the compact disks. Electroless nickel phosphorous (NiP) is a well established autocatalytic chemical technique has the advantage of providing uniform coating thickness on a surfaces of metals [6], alloys [7] and plastics [8]. Binary NiP alloy coating is obtained using sodium hypophosphite as reducing agent and without the use of electricity. Addition of surfactants [9] in NiP alloy coating crystallize the nano crystal of nickel there by increases the micro hardness. On the other side, the auto industry needs ternary alloys for excellent wear, corrosion and abrasion resistant surfaces. Inclusion of hard particles like oxides, carbides, ceramics and insoluble powders in NiP coatings were attempted [10]-[12] and found increases the hardness and wear resistance. Successful co-deposition of the included particle depends on size distribution [13], bath composition and inert nature of the particle. Co-deposition of Al_2O_3 particles in electoless nickel was attempted by many researchers [14], [15] and the co-deposition is still at the experimental stage. Adhesion is an interfacial property and important in determining the durability of thin coatings. In the field of surface chemistry, adhesion is a fundamental parameter and intimately related to wear. Adhesion measuring techniques can be classified into nucleation method and mechanical method.

In this study nano Al_2O_3 particles are co-deposited with NiP coatings and its surface morphology characterized. Adhesion, hardness and wear resistance for both NiP coatings and NiP-Al_2O_3 were compared.

II. EXPERIMENTAL DETAILS

Mild steel plate of thickness 6mm was prepared in the uniform size 20 mm × 20 mm. The samples were annealed at 200^oC for 8 hrs in a furnace for uniform microstructure. The steel plates were surface grinded and polished by 320, 800 and 1200 SiC papers. The surface roughness was maintained approximately 0.2 µm. Polished samples were cleaned in soap water and immersed in acetone and ensured for oil and dust free surface. The cleaned samples were activated in 10% HCl solution for 2 to 3 min before immersed in electrolyte solution. Coatings were synthesized on the prepared sample by immersion on the electrolyte solution and the chemical compositions of the solution were listed in Table.1. The pH of the electrolyte solution was maintained at 4-5. The solution was indirectly heated in an oil bath to temperature 87 ± 3^oC and was controlled using thermocouple. The samples were kept inside the electrolyte and the coating was done for period of 2 hours. The nano Al_2O_3 particles of size 50 to 100 nm were ultrasonicated in distilled water for 30 min before mixed in the electrolyte solution. The uniform distribution of nano Al_2O_3

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particles were maintained by providing an air agitation system in the electrolyte solution.

The surface morphology and surface characterization of NiP and NiP-Al_2O_3 coatings were done by scanning electron microscopy (FEG-SEM JEOL JSM-7001F) with Oxford EDX spectrum microanalysis system equipped with a light elements detector. X-ray diffraction was recorded using Bragg-Bernato configuration with Cu Kα1 radiation having a wavelength of 1.542 Å radiations.

A standard Rockwell C indentation was used to evaluate the adhesion of coating with substrate. The destructive quality of the indentation was compared by VDI 3198 norm and its principle is presented in Fig. 1. The indentations were made for a load of 150 kg to cause damage to the coating and an optical imaging technique was used to evaluate the test. The hardness of the coatings was measured using dynamic ultra micro indentation instrument (Shimadzu Duh211s) equipped with Berkovich indenter. The test was carried out at a maximum indentation load of 200 mN. The hardness of the coatings were calculated according to Oliver and Pharr's method [16]. The wear resistance of the coatings was determined by PLINT TE66 micro scale tester mounted with a steel ball under a constant load of 2.5 N with a sliding velocity 2.5 m/s. The wear volume was calculated for sliding distance of 160,320,480,640 and 800 m respectively using the equation

$$V \approx \frac{\pi b^4}{64R} \text{ for } b << R$$

where b is the wear crater diameter and R is the radius of the steel ball. The wear crater was characterized using optical microscope and scanning electron microscope.

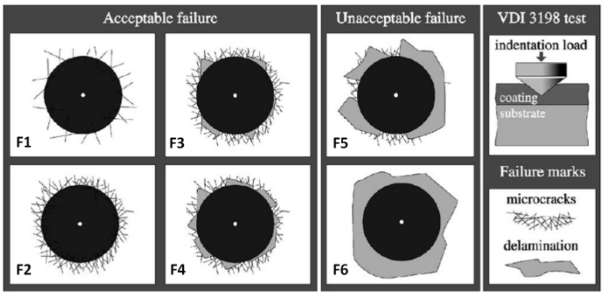


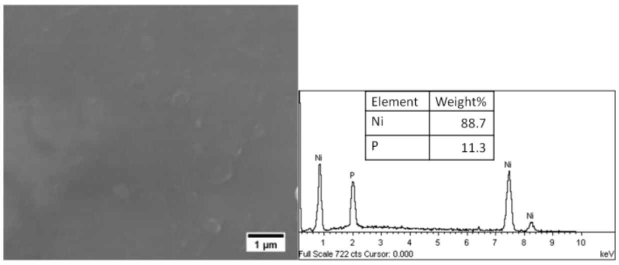
Fig. 1. Standard for VDI 3198 indentation test.

TABLE I: CHEMICAL COMPOSITION OF ELECTROLYTE SOLUTION

Coating bath composition	Concentration (g/l)
Nickel Chloride	40
Sodium Hypophosphite	30
Tri Sodium Citrate	25
Ammonium Chloride	50
Sodium Dodecyl Sulfate	0.6
Nano Al_2O_3	0.1

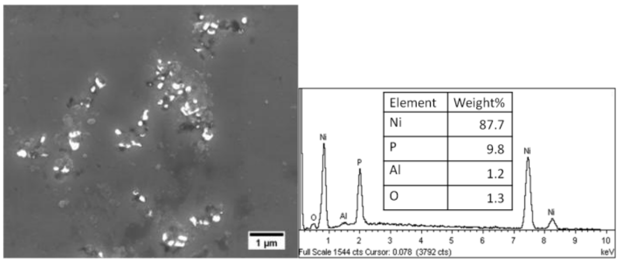
III. RESULT AND DISCUSSIONS

Fig. 2 shows the higher magnification SEM image of NiP coatings. It can be observed that surface of NiP coatings revel the formation of dense structure. The EDS spectrum shows that the phosphorus content is 11.3 weight % which is high phosphorus nickel coating with amorphous structure [17]. The properties of the electroless coatings are very sensitive to the amount of phosphorus content [18]. From SEM image shown in Fig. 3 it can be observed that the distribution of Al_2O_3 particles in NiPAl_2O_3 coatings. The co-deposition of Al_2O_3 particles increases the catalytic actives sites and thus increases reduction of nickel ions. The randomly adsorbed Al_2O_3 particles on the surface were covered by nickel due to further reduction reaction which leads to high surface roughness [19] and dim surface of the coating compared to NiP coatings. The presence of Al_2O_3 in the coatings was confirmed by EDS spectrum analysis and chemical analysis report showed Al_2O_3 is about 2.5 wt% with a reduction in phosphorus content to 9.8 wt%. Thus the decrease in phosphorous content is related to presence of alumina content in NiP coating which is in agreement with the micron size Al_2O_3 co-deposited in NiP matrix [20].



Element	Weight%
Ni	88.7
P	11.3

Fig. 2. SEM image and EDS spectrum of Ni-P coating.



Element	Weight%
Ni	87.7
P	9.8
Al	1.2
O	1.3

Fig. 3. SEM image and EDS spectrum of Ni-P-Al_2O_3 coating.

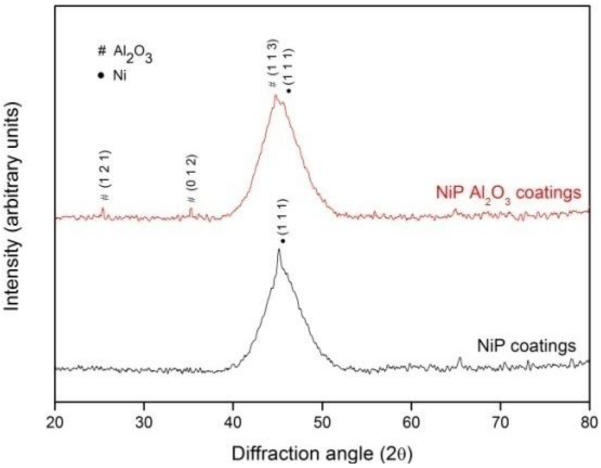


Fig. 4. X-ray diffraction of NiP and NiP Al_2O_3 coatings.

The X-ray diffraction pattern of Ni-P coatings and Ni-P-Al_2O_3 coatings are shown in Fig. 4. During deposition, the rate of diffusivity of phosphorous is small compared to nickel which results in lattice disorder in arrangement of atoms. This disorder leads to broader peak in X-ray diffraction of NiP and NiP-Al_2O_3 coatings. The broad peak range from 40-50^o

indicates that the both coatings has lattice disorder which affects the crstallinity of the coating. The disappearance of phosphorous peaks shows that phosphorus content in the coating is low because the deposition temperature is not sufficient to precipitate the phosphorous phases. The high intensity diffraction at 44.5° is a clear indication of Ni (111) plane which confirms the nano crystalline nature of the coatings. In NiP-Al_2O_3 coatings some small low intensity peaks of Al_2O_3 are observed which indicates the co-deposition of Al_2O_3 particles in NiP matrix.

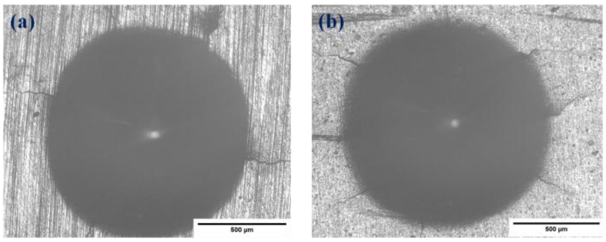


Fig. 5. Optical micrograph of Rockwell indentation test on (a) NiP coatings (b) NiP-Al_2O_3 coatings.

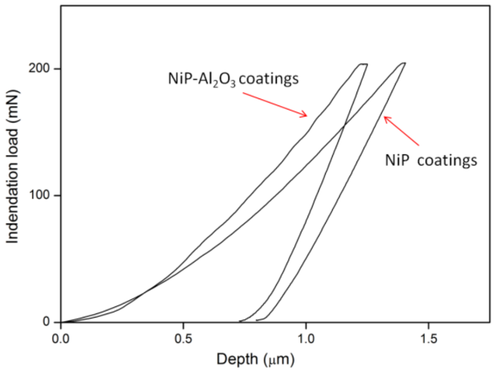


Fig. 6. Indentation load-depth curve on NiP and NiP-Al_2O_3 coating for indentation load 200 mN.

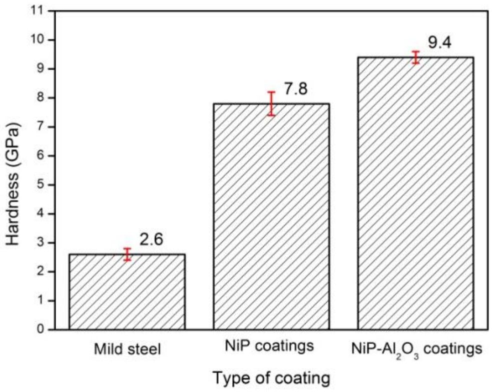


Fig. 7. Comparison of hardness of the substrate, NiP coatings and NiP Al_2O_3 coatings.

Adhesion measurement was done by using standard Rockwell hardness tester. The damage of the coating layer was compared with the VDI 3198 standard F1-F6 shown in Fig. 1. F1-F4 are the acceptable failures which defines sufficient adhesion and F5-F6 represents insufficient adhesion [21]. Optical micrograph images of indentation for NiP and NiP-Al_2O_3 coatings are given in Fig. 5. As seen in Fig. 5(a), there are few radial micro cracks observed at the perimeter of the indentation crater without any delamination in Ni-P coatings. The Fig. 5 (b) shows the indentation crater of NiP-Al_2O_3 coatings which has more number of radial cracks compared to NiP coatings however delamination on the coatings is not observed. The adhesion results were related to F1 and sufficient bonding is observed between the coating and substrate in both coatings.

The hardness of the coating was achieved using dynamic ultra micro indentation instrument. Fig. 6 shows the indentation load- depth curve for NiP and NiP Al_2O_3 coatings. Considering the maximum load of 200 mN, the maximum depth for NiP-Al_2O_3 coatings is 1.18 µm where as for NiP coatings the penetration depth is 1.4 µm. This decrease in depth of penetration is due to the co-deposited Al_2O_3 particles in NiP matrix which lead to decrease in contact area of the indenter with the coatings. The reduction in contact area results in hardness increase for NiP-Al_2O_3 coatings. In order to avoid the substrate hardness effect, the ratio between penetration depth to coatings thickness to be less than 0.1. As the average thickness of both coatings were 15 to 18 µm, the calculated hardness values has no effect on substrate [22].

Fig. 7 shows the hardness comparison of NiP and NiP-Al_2O_3 coatings. The reported hardness values represent the average and standard deviation of five replicates. As seen in Fig.7 there is abrupt increase in hardness value from substrate to NiP coating of about 7.8 MPa. The hardness value obtained for NiP-Al_2O_3 is 9.4 GPa. An increase in 1.6 GPa hardness value is due to the existence of hard Al_2O_3 particles which acts as a barrier to plastic deformation of NiP matrix [20].

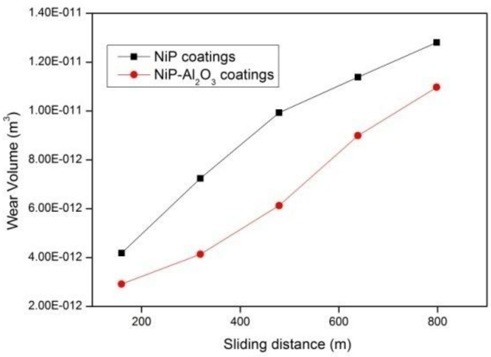


Fig. 8. Volume loss of NiP and NiP-Al_2O_3 coatings with varying sliding distance.

Fig. 8 shows the wear volume loss of NiP and NiP-Al_2O_3 coatings. It can be observed that the wear volume increases as the sliding distance increases in both coatings. However the wear loss for NiP-Al_2O_3 coatings remains less than that of NiP coatings. The co-deposition of Al_2O_3 particles resists the deformation during relative motion of steel ball over the coatings and hence the volume loss is smaller for NiP-Al_2O_3 coatings in all the sliding distances. This difference in wear volume is due to the high hardness of the coatings and the results are in agreement with SiC particles co-deposition in NiP matrix [23]. However the slope of the wear volume curve is not linear which might be due to the effect of material transfer between the coatings and steel ball.

Fig. 9 shows the variation of wear resistance over sliding distance of NiP and NiP-Al_2O_3 coatings. It is clearly seen that constant increase in the wear resistance of NiP coatings over the sliding distance. The relative movement of steel ball and NiP coatings leads to the material transfer and generation of wear debris. The wear debris oxidized and formed an oxide layer which acts as lubricant and increases the wear resistance of the NiP coating over the sliding distance. A rapid increase in wear resistance is observed for NiP-Al_20_3 coating till the sliding distance of 480 m and also observed that a slight decrease in wear resistance with a sliding distance of 800 m. As the interfacial bond between NiP matrix and Al_2O_3 particles is good which results in maximum wear resistance upto a sliding distance of 480 m. But further increase in sliding distance leads to formation of wear debris which consists of Al_2O_3 particles. The presence Al_2O_3 particles in wear debris acts as abrasive particles there by the wear resistance of NiP-Al_2O_3 coatings got reduced. However the formation of oxide layer resists the wear loss and detained decrease in wear resistance.

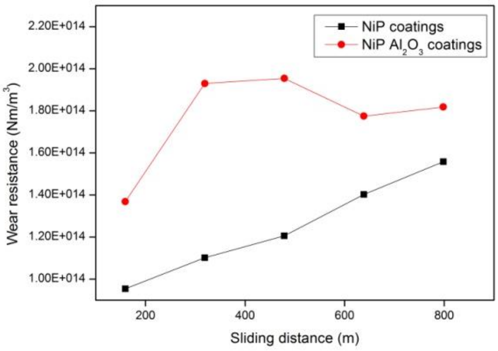


Fig. 9. Wear resistance of NiP and NiP-Al_2O_3 coatings with varying sliding distance.

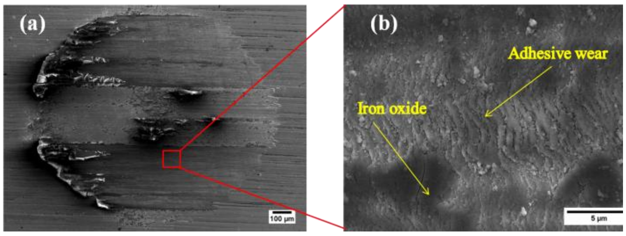


Fig. 10. SEM images of wear crater NiP coating (a) for a sliding distance of 800 m (b) at higher magnification.

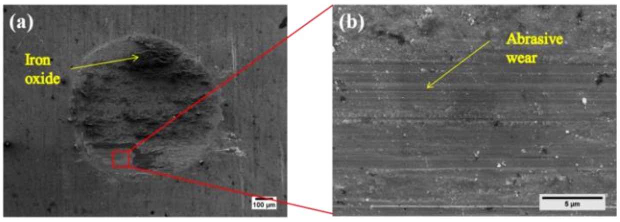


Fig. 11, SEM images of wear crater NiP-Al_2O_3 coating (a) for a sliding distance of 800 m (b) at higher magnification.

The scanning electron micrograph image of wear crater for NiP coatings is shown in Fig. 10. For larger sliding distance, which is 800 m in Fig. 10(a) the top surface is completely worn out. During initial rotation of steel ball, a perfect contact between the surfaces took place which lead to shear and deformation of the coating. The deformation results in material detachment, debris generation and material transfer. The transferred materials and wear debris are easily carried out along the rotation of steel ball but most of the particles firmly bound and entrapped between steel ball and coating. The entrapped particles oxidized and observed as ridges. The formed ridges acts as lubricating layer and increases the wear resistance of the coating. The closer observation of wear crater in Fig. 10(b) of NiP coating indicates plastic deformation of the coating which could form wear debris by an adhesive wear mechanism.

A general view of wear crater on NiP-Al_2O_3 coating is shown in Fig. 11. It is observed that wear crater is typical smaller diameter than NiP wear crater for the same sliding distance of 800 m. There are more ridges of iron oxide observed in Fig. 11(a) which increases the wear resistance of the coating. During the wear test process the co-deposited Al_2O_3 particles have reduced the direct contact of steel ball with coating. This reduction in contact not only reduces the wear but increases the more amount of material transfer from steel ball. The magnified wear crater image in Fig.11 (b) reveals that abrasive grooves and scuffing of coating with absence of prominent plastic deformation and the wear morphology of NiP-Al_2O_3 coatings. The formation of grooves can be associated with the presence of hard Al_2O_3 particles between steel ball and the coating surface. Initially the co-deposited Al_2O_3 particles were pressed in NiP matrix due the rotating action of steel ball. The pressed in particles were extensively form interfacial bond with NiP matrix which results in increase of wear resistance of the NiP-Al_2O_3 coatings. During continuous relative motion the Al_2O_3 particles detached from the coating giving rise to a negative result by scratching and ploughing of the coating surface which shows the wear mechanism is dominated with abrasive wear.

IV. CONCLUSIONS

Electroless NiP shows some attractive properties of high hardness and better adhesion however their properties further enhanced by co-deposition of second phase Al_2O_3 particles. Based on coating preparation and analysis of results using characterization and mechanical tests, the following conclusions have been obtained.

- Distribution of Al_2O_3 particles on NiP coatings were clearly observed on the scanning electron micrograph images. The EDX results revel that decrease in phosphorus content from 11.3% to 9.8% due to the co-deposition of Al_2O_3 particle.
- Surface hardness improved from 2.6 GPa to 7.8GPa (increase in 200%) due to the deposition of NiP coating on mild steel. Further improvement in hardness to 9.4 GPa (increase in 20.5%) due to co-deposition of Al_2O_3 particles with NiP coatings.
- Adhesion measurement through indentation techniques shows that absence of delamination in both NiP and NiP-Al_2O_3 coatings and mild steel substrate is highly adherent to coating.
- The co-deposition of Al_2O_3 particles results in decrease in wear volume and increase in wear resistance during dry siding conditions. The wear morphology shows that adhesive wear mechanism in NiP coatings where as combined adhesive and abrasive wear mechanism in NiP-Al_2O_3 coatings.

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